

COOPERATIVE CALIBRATION AND ANALYSIS OF CEMENT CLINKER PHASES

**FILE COPY
DO NOT REMOVE**

L. Struble*

**U.S. DEPARTMENT OF COMMERCE
National Institute of Standards
and Technology
Center for Building Technology
Gaithersburg, MD 20899**

H. Kanare

**Construction Technology Laboratories, Inc.
Skokie, IL 60077**

***Present address:
University of Illinois
Department of Civil Engineering
Urbana, IL 61801-2397**

**U.S. DEPARTMENT OF COMMERCE
Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Raymond G. Kammer, Acting Director**

NIST

COOPERATIVE CALIBRATION AND ANALYSIS OF CEMENT CLINKER PHASES

L. Struble*

**U.S. DEPARTMENT OF COMMERCE
National Institute of Standards
and Technology
Center for Building Technology
Gaithersburg, MD 20899**

H. Kanare

**Construction Technology Laboratories, Inc.
Skokie, IL 60077**

***Present address:
University of Illinois
Department of Civil Engineering
Urbana, IL 61801-2397**

September 1989



**U.S. DEPARTMENT OF COMMERCE
Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Raymond G. Kammer, Acting Director**

ABSTRACT

An interlaboratory calibration and analysis has been carried out by ASTM Task Group C01.23.01 to assess the use of quantitative X-ray diffraction analysis to determine the proportion of phases in portland cement clinker. This interlaboratory test provides an estimate of precision and bias in the quantitative phase analysis of some clinker phases in mixtures prepared using calibrating phases. These estimates of precision and bias will be incorporated in a proposed standard test method on quantitative phase analysis of cement and clinker currently being developed by the task group.

Table of Contents

	<u>Page</u>
ABSTRACT	iii
1. INTRODUCTION	1
2. PARTICIPANTS	2
3. CALIBRATION PHASES	2
3.1 Cubic C ₃ A	2
3.2 Orthorhombic C ₃ A	3
3.3 MgO	3
3.4 C ₄ AF	3
4. CALIBRATION MIXTURES	3
5. ANALYTICAL PROCEDURES	9
6. RESULTS ON UNKNOWN MIXTURES	11
7. CONCLUSIONS	18
8. ACKNOWLEDGEMENTS	19
APPENDICES	
Appendix 1. Laboratories Participating in Cooperative Calibration	20
Appendix 2. Summary of Results	21
Appendix 3. Statistical Analysis	32

List of Tables

	<u>Page</u>
Table 1. Calibration mixtures	6
Table 2. Proportions used in unknown mixtures	7
Table 3. Peaks recommended for QXRD analysis	10
Table 4. Summary of statistical analysis	17
Table 3-1. QXRD results for statistical analysis	36
Table 3-2. Cell averages	37
Table 3-3. Cell standard deviations	38
Table 3-4. Between-laboratory consistency statistic values	39
Table 3-5. Within-laboratory consistency statistic values	40
Table 3-6. Summary of precision parameters	41
Table 3-7. Cell averages excluding Laboratory 3	42
Table 3-8. Summary of precision parameters excluding Laboratory 3	43
Table 3-9. Linear regression, standard deviation versus average	44

List of Figures

	<u>Page</u>
Figure 1. Particle size distribution curve for cubic C ₃ A calibration phase	4
Figure 2. Particle size distribution curve for MgO calibration phase	5
Figure 3. Particle size distribution curve for calibration mixture No. 1	8
Figure 4. Results from QXRD analysis of cubic C ₃ A showing actual value for Unknown #1 (lower line) and Unknown #2 (upper line)	12
Figure 5. Results from QXRD analysis of orthorhombic C ₃ A showing actual value for Unknown #1 (lower line) and Unknown #2 (upper line)	13
Figure 6. Results from QXRD analysis of C ₃ A (cubic plus orthorhombic) showing actual value for Unknown #1 (lower line) and Unknown #2 (upper line)	14
Figure 7. Results from QXRD analysis of C ₄ AF showing actual value for Unknown #1 (upper line) and Unknown #2 (lower line)	15
Figure 8. Results from QXRD analysis of MgO showing actual value for Unknown #1 (upper line) and Unknown #2 (lower line)	16
Figure 3-1. Level of h-value for each laboratory (critical values indicated by upper and lower horizontal lines)	33
Figure 3-2. Level of k-value for each laboratory (critical value indicated by horizontal line)	34
Figure 3-3. Standard deviation versus average value (relative to the mixture) for each phase in each unknown mixture, showing results of linear regression analysis (Table 3-9)	35

1. INTRODUCTION

A proposed test method to determine the proportion of certain phases in portland cement or clinker using quantitative X-ray diffraction (QXRD) is currently under development by ASTM Task Group C01.23.01, chaired by Leslie Struble. The approach is similar to the approach used in developing performance requirements for rapid analytical methods for ASTM C 114, Standard Methods for Chemical Analysis of Hydraulic Cement. The approach specifies certain general aspects of the analytical procedure, but leaves optional most of the specific details of the analysis. However, the approach specifies the levels of precision and bias that must be met for the particular selected analytical method to qualify. Detailed methods will be described that have been shown to meet these levels, including the methods used in the round-robin analyses to determine the specified precision and accuracy levels.

To develop the precision and bias levels for the test method, the task group is carrying out a number of interlaboratory analyses. These analyses utilize two groups of phases. The first group, tricalcium aluminate (C_3A^1), tetracalcium aluminoferrite (C_4AF), and magnesium oxide (MgO), are the subject of two interlaboratory analyses. The first, described in the present report, is a cooperative calibration using mixtures of individual phases prepared and made available by the Construction Technology Laboratories (CTL). This cooperative calibration will be followed by a round-robin analysis of standard clinkers made available as Research Materials by the Office of Standard Reference Materials (OSRM) of the National Institute of Standards and Technology (NIST).

¹The following abbreviations (common in the cement and concrete literature) are used: C for CaO, A for Al_2O_3 , F for Fe_2O_3 , and S for SiO_2 .

The cooperative calibration included three mixtures in known proportions, to determine the relationship between the proportion of each phase and its XRD intensity, and two mixtures in unknown proportions. The results obtained for the two unknown mixtures in the cooperative calibration have been analyzed according to procedures in ASTM E 691, Standard Practice for Conducting an Interlaboratory Test Program To Determine the Precision of Test Methods. Precision and bias levels determined from this statistical analysis will be incorporated subsequently in the test method.

The group of phases selected for this cooperative effort simulates the phases typically found in a salicylic acid or maleic acid extracted clinker. It is expected that the recommended analytical scheme in the test method will include two analyses: analysis before extraction for proportions of C_3S and C_2S , and analysis after extraction for proportions of C_3A , C_4AF , and MgO .

2. PARTICIPANTS

Fifteen laboratories elected to participate in this effort. The participating laboratories are listed in Appendix 1. Nine laboratories have reported results. All results are reported anonymously (using a Laboratory Number). If additional results become available, this report will be amended.

3. CALIBRATION PHASES

Three phases were prepared at CTL for this calibration: cubic C_3A , orthorhombic C_3A (stabilized by Na), C_4AF , and MgO . Each phase was prepared using reagent-grade chemicals.

3.1 Cubic C_3A

Cubic C_3A was prepared using 658.4 g $CaCO_3$ and 341.6 g $Al(OH)_3$. These were ground in a 4-L pebble mill with 500 mL distilled water for 20 min. The ball charge consisted of a 50:50 mixture of 9.5 mm (3/8") and 19.1 mm (3/4") aluminum oxide balls. The slurry was dried in a forced air oven. The dried powder mixture was pressed into pellets 52 mm diameter under approximately 7,000 kg (total load). The pellets were placed in platinum dishes and sintered by heating at 1450°C for 3 hrs. The sintered mass was crushed to pass a 0.60 mm (No. 30) sieve, then ground dry in a pebble mill for 60 min. It was repelletized, reheated at 1450°C for 3 hrs, and ground in a pebble mill to a Blaine fineness of 3050 cm^2/g . Particle size analysis using a

Sedigraph² (Fig. 1) indicates that 95 percent of the material was finer than 50 μm .

3.2 Orthorhombic C_3A

Orthorhombic C_3A was prepared using 31.0 g Na_2CO_3 , 233.0 g CaCO_3 , and 136.1 g $\text{Al}(\text{OH})_3$. These were processed as described above for cubic C_3A , but were heated at the following schedule: 1.5 hrs at 1400°C then 1.0 hr at 1450°C.

3.3 MgO

The MgO was prepared using MgCO_3 . This was pelletized and heated for 2 hrs at 950°C, then 0.5 hrs at 1500°C. It was ground in a pebble mill to a Blaine fineness of 4620 cm^2/g . The particle size distribution is shown in Fig. 2.

3.4 C_4AF

A sample of C_4AF that had been prepared previously at CTL was ground in a pebble mill until it passed a 75 μm (No. 200) sieve. Details on the preparation of this phase are not available.

4. CALIBRATION MIXTURES

Three calibration mixtures in known proportions and two mixtures in unknown proportions were prepared from the calibration phases. The proportions are listed in Table 1 for the calibrating mixtures, and in Table 2 for the unknown mixtures.

The mixing process had a target fineness level of approximately 95 percent finer than 10 μm . Mixtures were ground using a tungsten carbide swing mill with tungsten carbide ring and puck. Ethylene glycol (reagent grade) was added as a grinding aid, using 50 μL per batch. Mixtures were ground 1 min at 800 rpm. The mixtures were brushed into glass vials and sealed. The particle size distribution of a calibration mixture is shown in Fig. 3. According to this distribution, the mixture is somewhat coarser than the target (70 percent, rather than 90 percent, finer than 10 μm).

²Certain trade names and company products are identified to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION Cubic C₃A ASTM C01.23.01 QXRD Task Group

DATE 1/31/89

Density 3.03 g/cc LIQUID A12

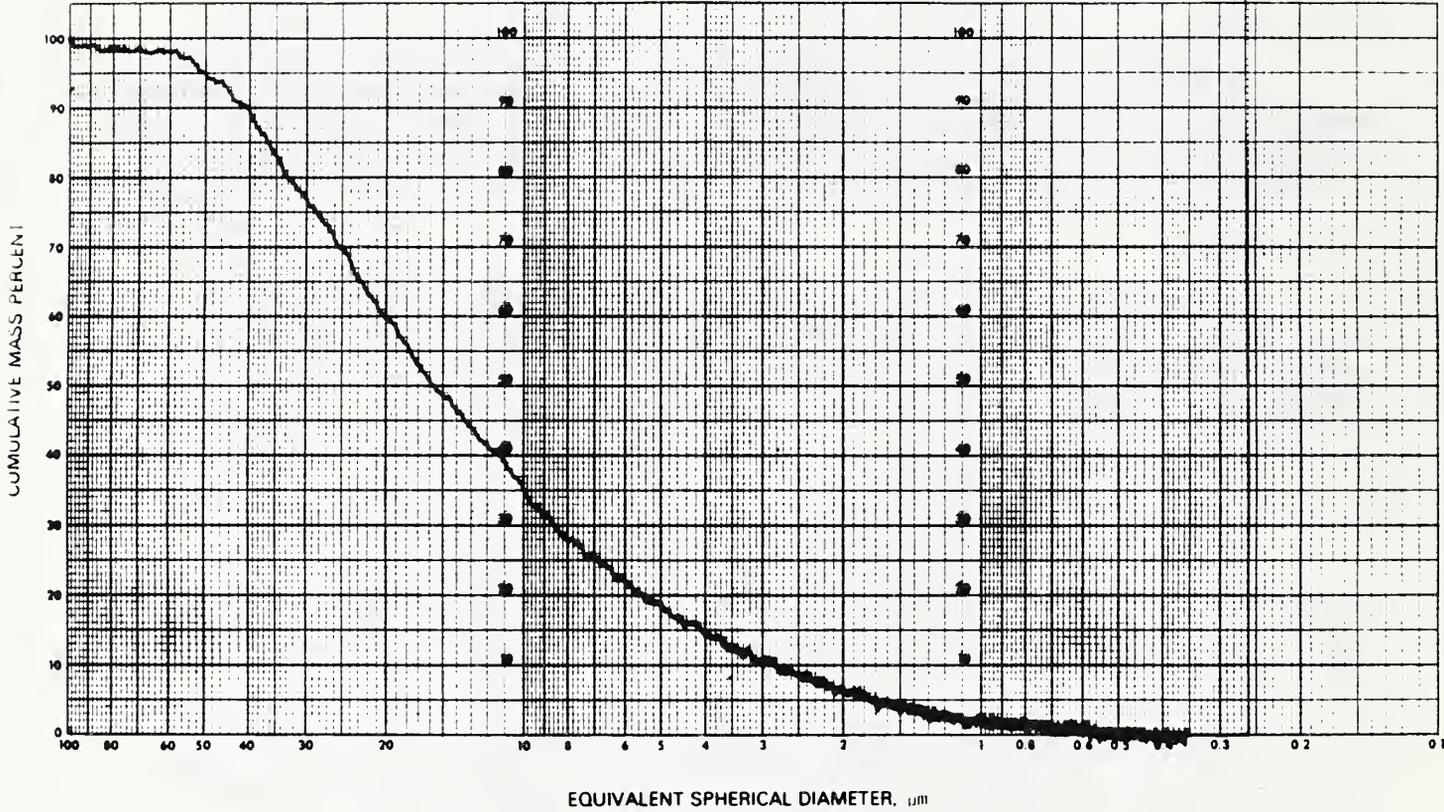
Density 0.805 g/cc Viscosity 3.71 cp

BY Linda M. Hills

Preparation 0.3 g sample + 27 mL Sedisperse + 4 min. ultrasonic dispersion

TEMPERATURE 33 °C

RATE 508 START DIA 100 μm



Form 500 42701

Figure 1. Particle size distribution curve for cubic C₃A calibration phase.

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION MgO ASTM C01.23.01 QXRD Task Group
Density 3.58 g/cc LIQUID A12 Density 0.805 g/cc Viscosity 3.71 cp
Preparation 0.3 g sample + 27 mL Sedisperse + 4 min. ultrasonic dispersion

DATE 1/31/89
BY Linda M. Hills
TEMPERATURE 33 C
RATE 637 START DIA 100 μ m

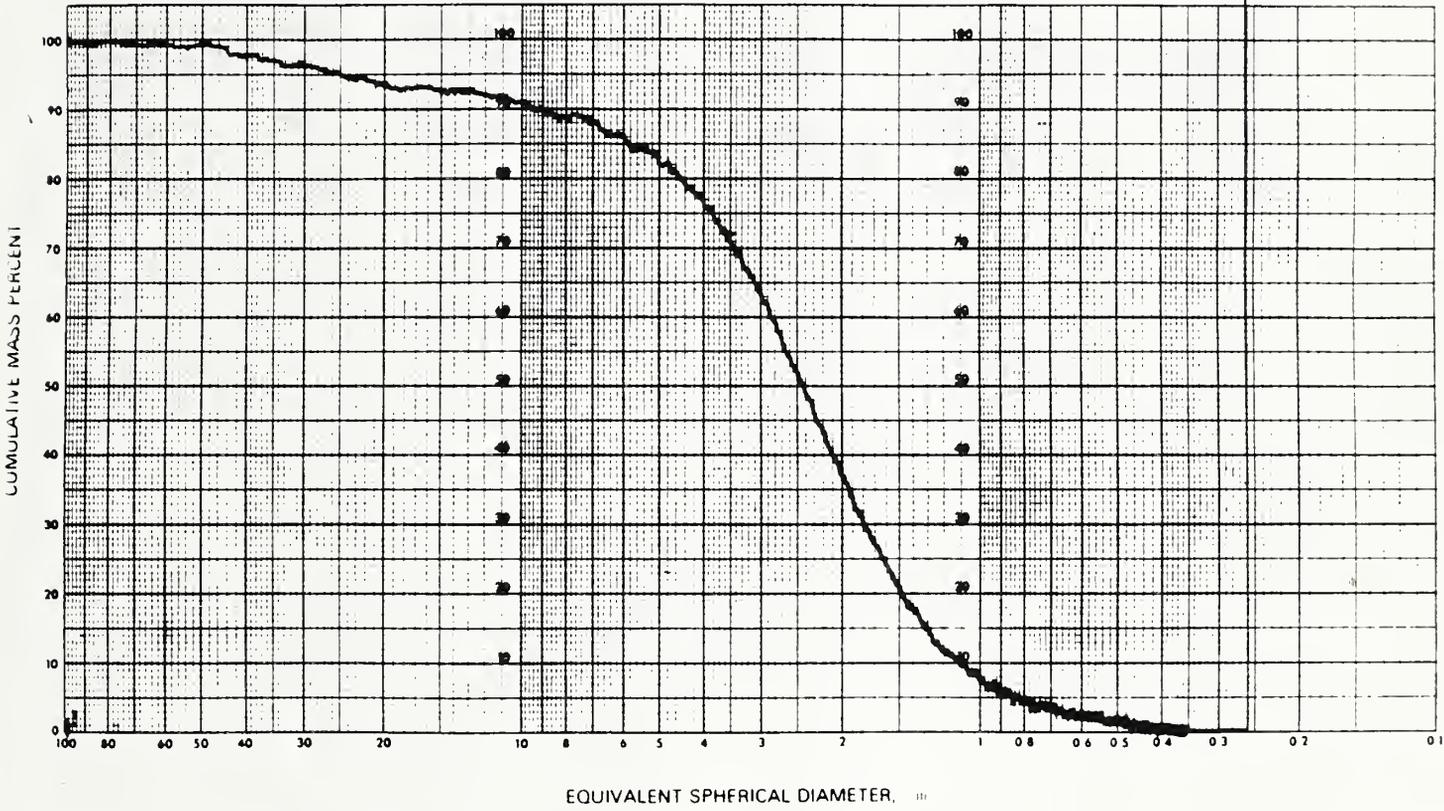


Figure 2. Particle size distribution curve for MgO calibration phase.

Table 1
Calibration Mixtures

	percent of mixture			percent of clinker		
	A	B	C	A	B	C
C ₃ A						
Cubic	65	11	29	11.05	1.87	4.93
Orthorhombic	0	51	7	0.0	8.67	1.19
C ₄ AF	35	11	60	5.95	1.87	10.20
MgO	0	27	4	0.0	4.59	0.68

Table 2

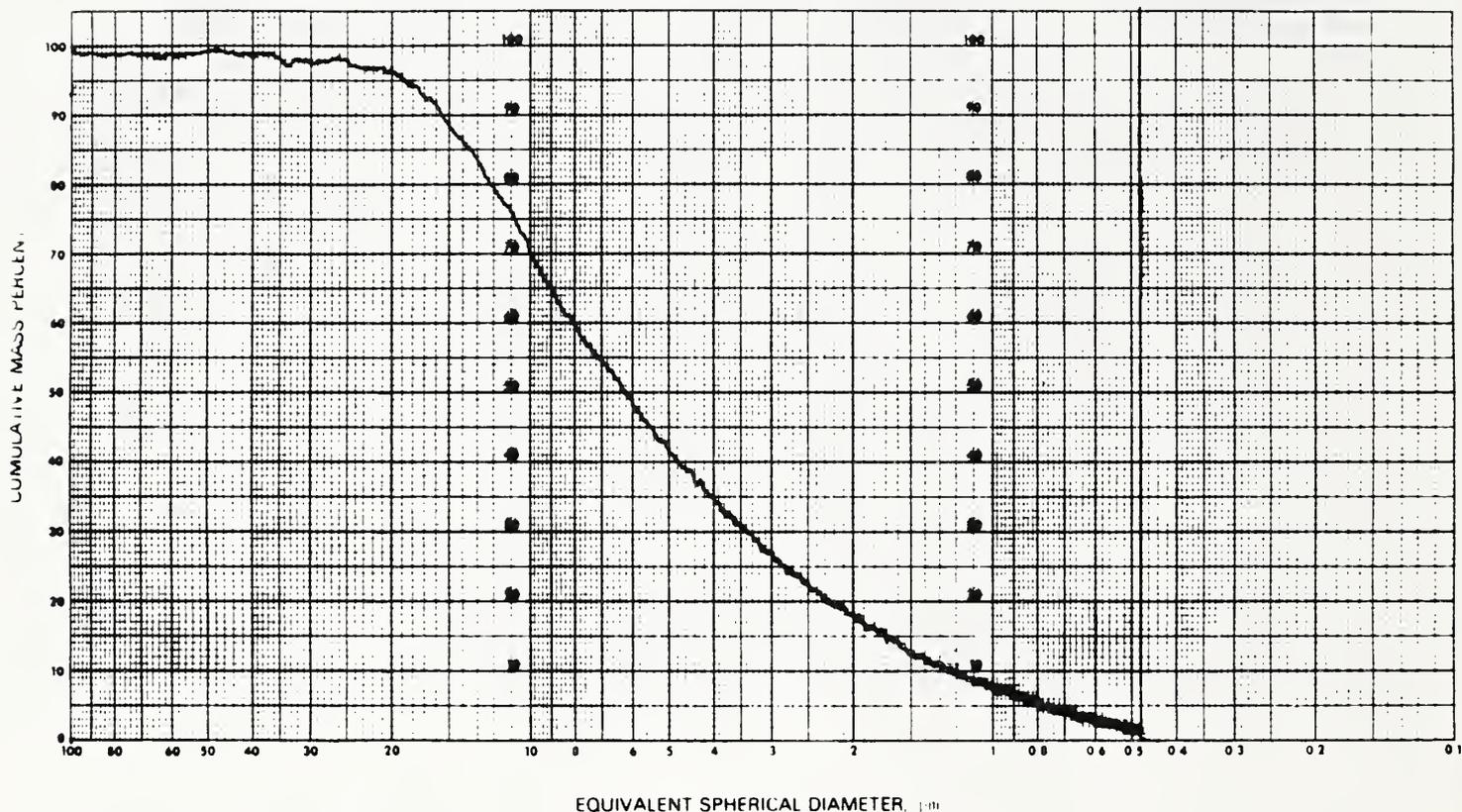
Proportions Used in Unknown Mixtures

	percent of mixture (% of extraction residue)		percent of clinker	
	Unknown 1	Unknown 2	Unknown 1	Unknown 2
orthorhombic C_3A	0.0	7.0	0.00	1.05
cubic C_3A	20.0	63.0	3.00	9.45
C_4AF	58.0	26.0	8.70	3.90
MgO	22.0	4.0	3.30	0.60

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION Mixture No. 1 - ASTM C01.23.01 Task Group on QXRD
Density 3.15 g/cc LIQUID Al2 Density 0.810 g/cc Viscosity 3.89 cp
Preparation 0.3 g sample + 27 mL Sedisperse + 4 min ultrasonic dispersion

DATE 6/11/87
BY Linda M. Hills
TEMPERATURE 32 C
RATE 510 START DIA 100 μ m



Form 500/42701

Figure 3. Particle size distribution curve for calibration mixture No. 1.

It was required that participants use an internal standard. The internal standard was specified to be a pure, stable material, 95 percent of which was finer than 10 μm . The choice of material was left up to each participant; recommended materials were NIST SRM 640a (silicon) or one of the materials included in SRM 674 (especially the TiO_2). Recommended proportions were 0.12000 g internal standard per 1.00000 g calibration or unknown mixture (corresponding to 0.0200 g internal standard per 1.0000 g clinker).

5. ANALYTICAL PROCEDURES

The calibration and unknown mixtures were mixed with the internal standard material by the participants. Participants were required to weigh out each mixture and to blend with the internal standard. Components were weighed to the nearest 0.0001 g using an analytical balance. They were blended to provide homogeneous specimens; the recommended method was to blend each calibration mixture for approximately 10 minutes using a vibratory-type mill, with approximately 5 ml of a non-aqueous solvent such as Freon for each gram of powder, and with appropriate grinding media. Suitable mills include the Spex Mixer Mill.

Participants were instructed to use their normal procedures for specimen preparation and for collecting the diffraction patterns. The operating parameters for collecting diffraction patterns are difficult to specify, as they depend on the particular instrument. The parameters recommended for accurate and reproducible intensity measurements were slow scanning speeds and moderately large receiving-slit widths.

Participants were also instructed to scan and measure the intensities of as many peaks as possible for each phase, including but not limited to those peaks listed in Table 3. Peak intensities were to be measured using the integrated intensity of the peak above the background.

Participants then developed calibration curves relating the measured intensity of the XRD peaks for each phase, relative to the intensity of the internal standard peak, to the known proportion of the phase. This could be done graphically, or using a computer to determine the best-fitting (i.e. least squares) line.

As a preliminary assessment of the calibration, each participant used the calibration results to determine the proportion of each phase in two mixtures prepared using the same calibrating phases. The participants did not know these proportions (Table 2). The two unknown mixtures were prepared and analyzed in triplicate (i.e., three replicate preparations of

Table 3

Peaks Recommended for QXRD Analysis

Phase	hkl	d-spacing	(2 θ) using Cu K α
cubic C ₃ A	(023)	0.4236 nm	21.0°
	(213)	0.4083 nm	21.8°
orthorhombic C ₃ A	(113)	0.4210 nm	21.1°
C ₄ AF	(130)	0.3654 nm	24.3°
MgO	(200)	0.2106 nm	42.9°

Note: The intensity of the (113) peak of orthorhombic C₃A must be corrected for any contribution from the (023) peak of cubic C₃A. The intensity of the (023) peak is calculated by multiplying the (213) peak by a correction factor. The correction factor is determined using Sample A by calculating the intensity ratio of the (023) peak to the (213) peak for cubic C₃A.

each specimen). In order to improve the statistical reliability of the results, the replicate specimens of the two unknown mixtures were interleaved (i.e., a specimen of one unknown was prepared and analyzed, than a specimen of the other unknown prepared and analyzed, etc.). The same procedures were followed that had been used in the calibration mixtures for collecting diffraction patterns and measuring integrated peak intensities. The amount of each phase in each replicate of the two unknown samples was then calculated using the calibrations obtained in the first part of this analysis.

6. RESULTS ON UNKNOWN MIXTURES

The individual results reported by each laboratory are listed in Appendix 2 and summarized graphically in Figs. 4 through 8.

The results were analyzed statistically to estimate precision and bias. The objective of the statistical analysis was to provide precision and bias levels to include in the subsequent proposed standard test method. The precision analysis followed the procedure of ASTM E 691. The statistical analysis is described in detail in Appendix 3 of this report. There were 8 materials (each phase in each unknown were treated as a separate material), and 7 laboratories³.

The critical values of the consistency statistics (h and k) were exceeded only by one laboratory (Laboratory 3). Examination of the XRD patterns provided by this laboratory showed a considerably higher noise level and lower intensity ratio of peak/background compared to patterns of other participating laboratories. Therefore, it was decided that the results reported by Laboratory 3 were not as consistent as expected from this analysis, and the final statistical analysis did not include results from Laboratory 3.

The statistical analysis from Appendix 3 is summarized in Table 4. Note that results in Appendix 3 are expressed as a percent of the mixture, whereas results in Table 4 have been converted to a percent of clinker⁴.

The average measured values (Table 4) agree well with the known values (Table 2). In nearly every instance these values differ by less than the reproducibility standard deviation (s_R in

³Laboratories 4 and 7 did not report replicate results and therefore could not be used in this statistical analysis.

⁴For this calculation, each mixture was considered to represent 17 percent of a hypothetical clinker.

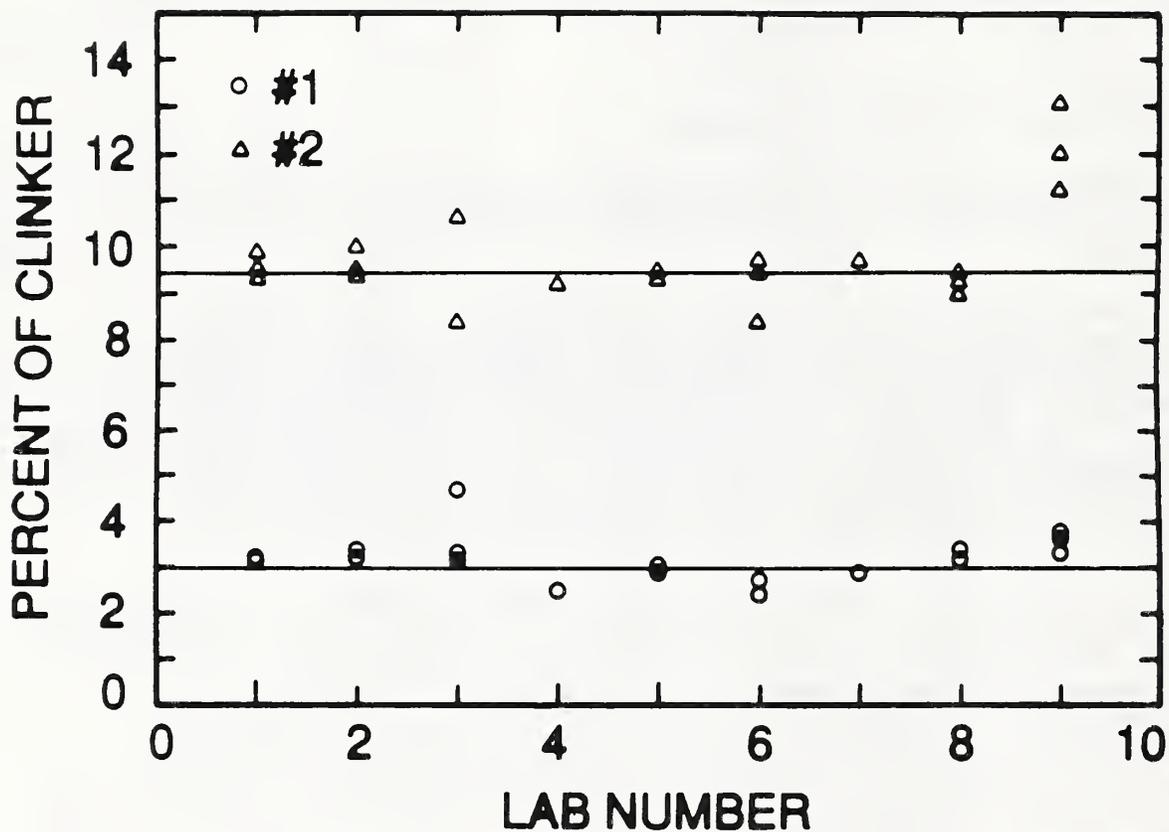


Figure 4. Results from QXRD analysis of cubic C₃A showing actual value for Unknown #1 (lower line) and Unknown #2 (upper line).

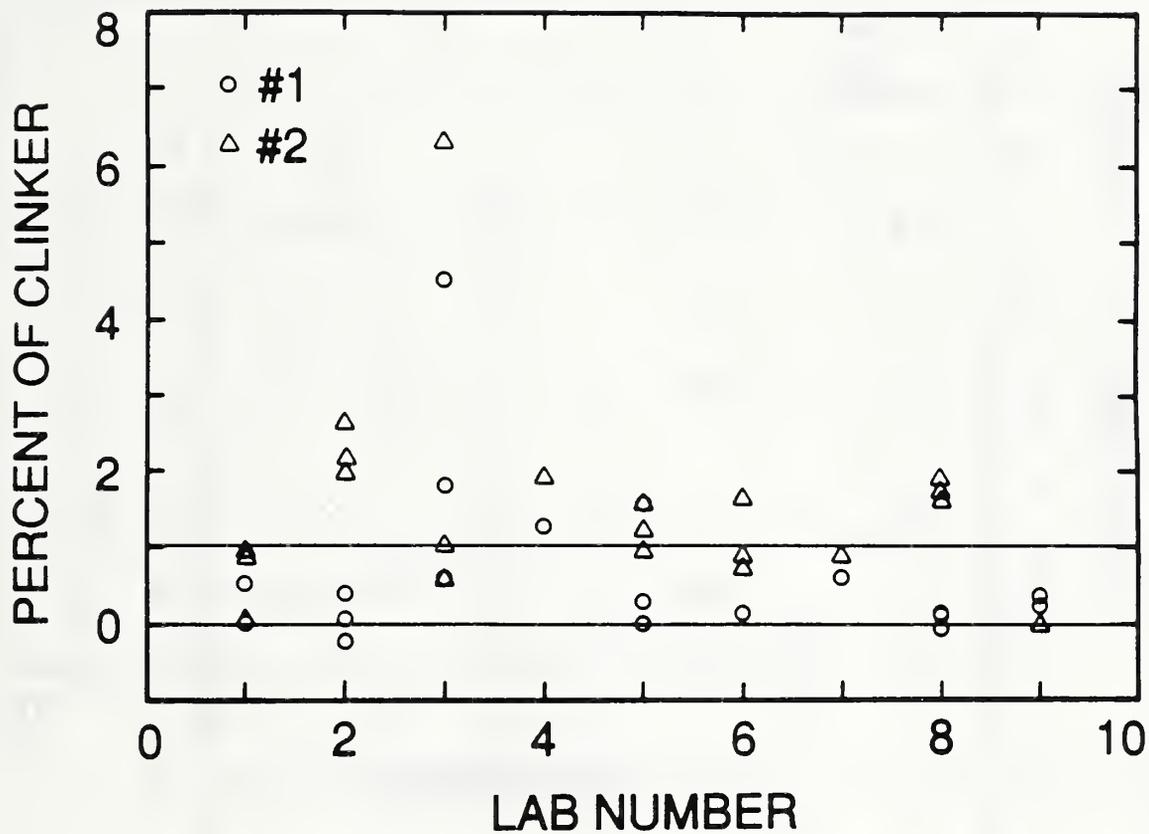


Figure 5. Results from QXRD analysis of orthorhombic C_3A showing actual value for Unknown #1 (lower line) and Unknown #2 (upper line).

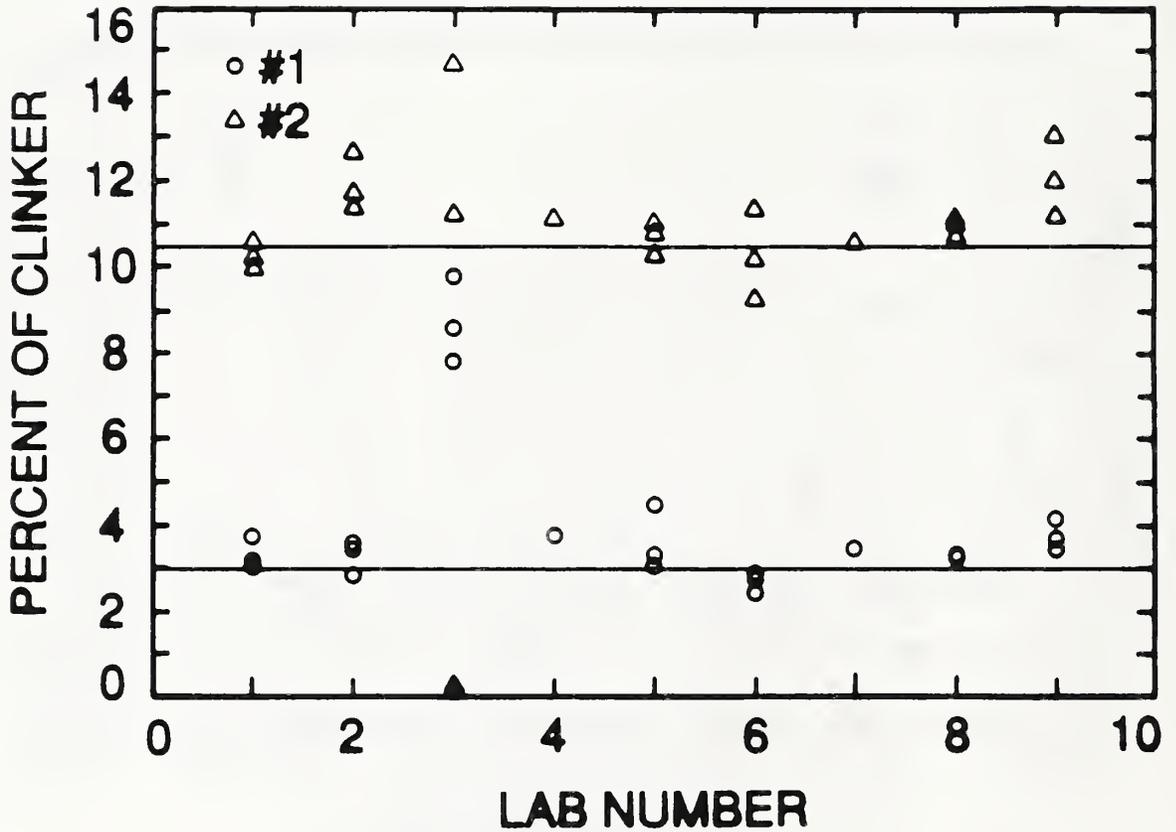


Figure 6. Results from QXRD analysis of C_3A (cubic plus orthorhombic) showing actual value for Unknown #1 (lower line) and Unknown #2 (upper line).

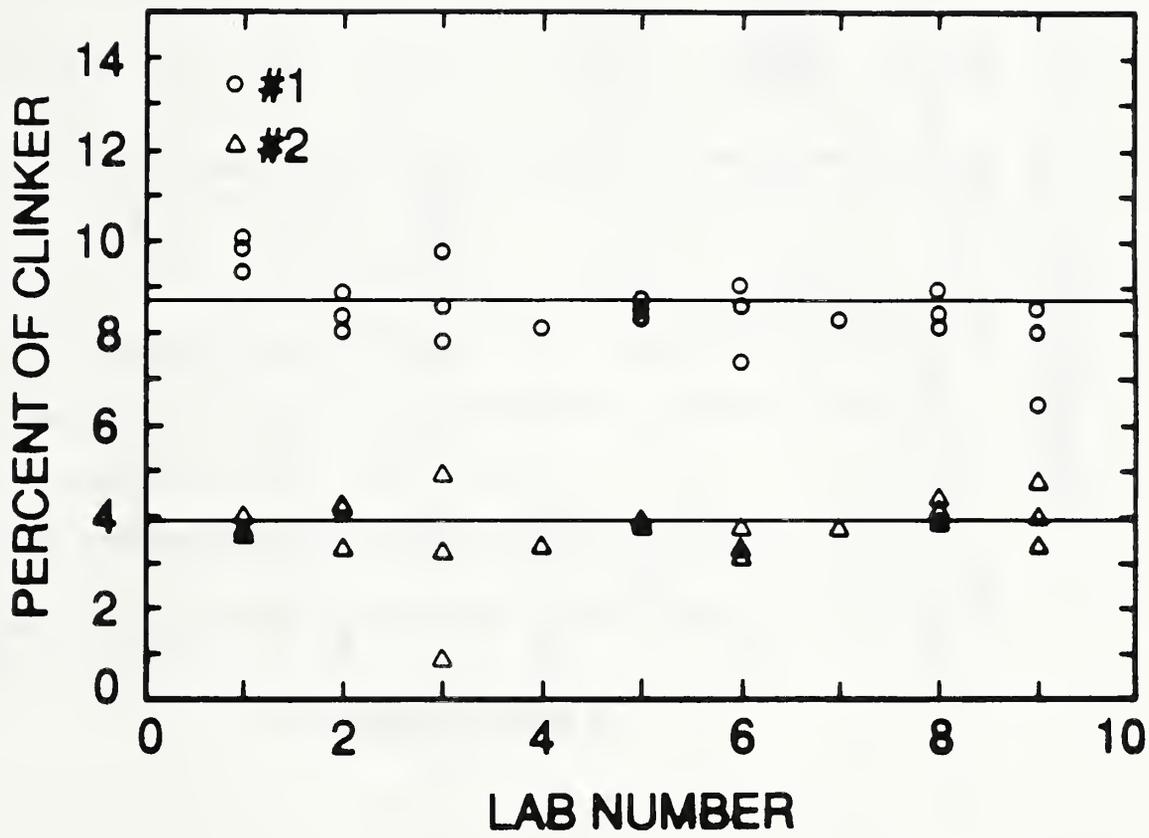


Figure 7. Results from QXRD analysis of C_4AF showing actual value for Unknown #1 (upper line) and Unknown #2 (lower line).

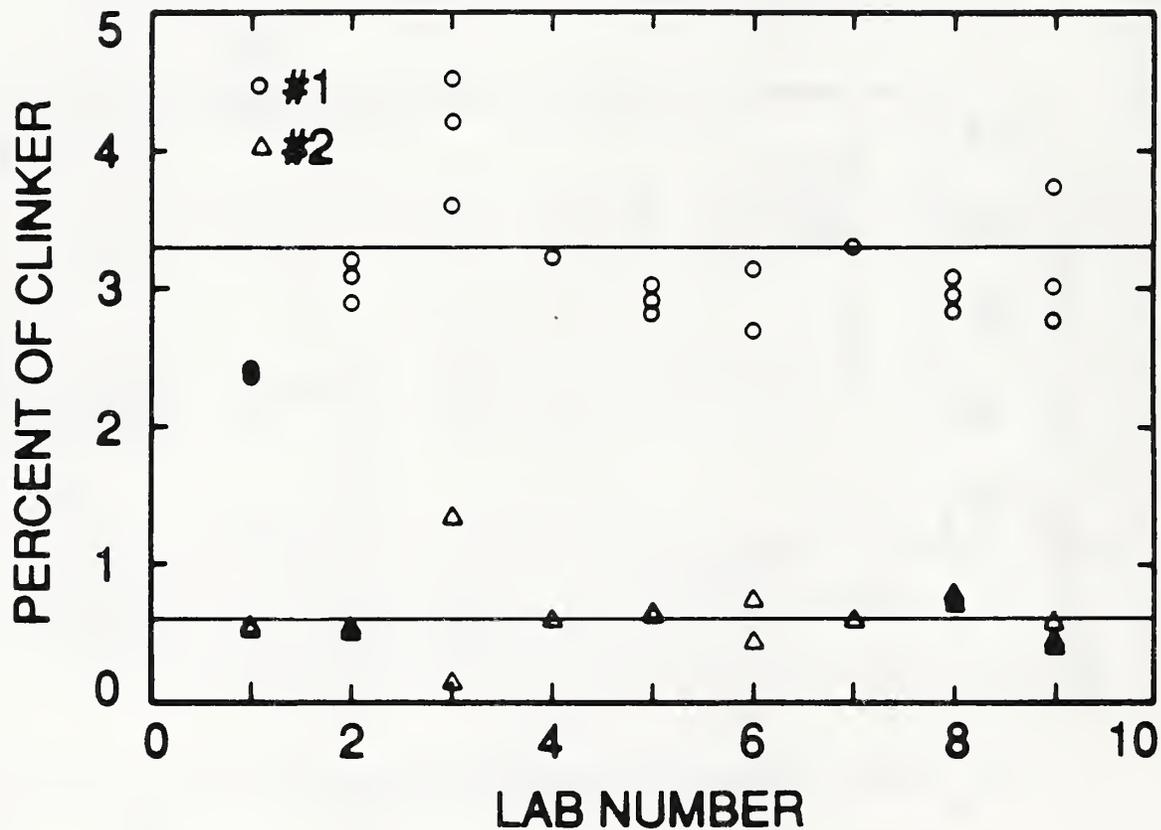


Figure 8. Results from QXRD analysis of MgO showing actual value for Unknown #1 (upper line) and Unknown #2 (lower line).

Table 4

Summary of Statistical Analysis
(percent of clinker)

Phase	Unknown	Average	Standard deviation		95% Limit	
			s_r^a	s_R^b	r^c	R^d
orthorhombic C_3A	1	0.22	0.45	0.45	1.25	1.25
	2	1.34	0.39	0.97	1.10	2.71
cubic C_3A	1	3.51	0.18	0.39	0.51	1.08
	2	11.21	0.59	1.35	1.65	3.77
C_4AF	1	9.65	0.72	0.98	2.03	2.74
	2	4.39	0.45	0.47	1.27	1.32
MgO	1	3.31	0.28	0.38	0.78	1.08
	2	0.67	0.09	0.14	0.26	0.38

^arepeatability (within laboratory) standard deviation

^breproducibility (between laboratory) standard deviation

^crepeatability limit (2.8 times s_r)

^dreproducibility limit (2.8 times s_R)

Table 4). Thus there appears to be no bias in these test results.

Based on the estimated levels of repeatability standard deviation (s_r in Table 4), the limit for 95 percent repeatability (r in Table 4) averaged 1.1 percent (relative to the total clinker) and ranged from 0.3 percent to 2.0 percent for the phases in this interlaboratory test. Likewise, the limit for 95 percent reproducibility (R in Table 4) averaged 1.8 percent (relative to the total clinker) and ranged from 0.4 percent to 3.8 percent.

These precision indices will form the basis for repeatability and reproducibility levels to be specified in the proposed standard test method being developed by Task Group C01.23.01 for analysis of cubic C_3A , orthorhombic C_3A , C_4AF , and MgO . Single values for repeatability and reproducibility indices are reported here. However, the standard deviation levels and corresponding precision indices are not necessarily equal for all phases. To estimate these levels for each individual phase, additional unknown mixtures are required in the cooperative calibration and analysis. The interlaboratory tests planned by the task group may provide sufficient data to estimate individual levels.

7. CONCLUSIONS

Calibrations have been carried out for quantitative X-ray diffraction analysis of cubic C_3A , orthorhombic C_3A , C_4AF , and MgO . The calibrations were then used to analyze for these phases in two unknown mixtures. In nearly every instance, the measured value in the unknown mixture differed from the known value by less than the reproducibility standard deviation. Thus there appears to be no bias in these results.

Based on these results, the following repeatability and reproducibility levels may be specified for analyses of cubic C_3A , orthorhombic C_3A , C_4AF , and MgO in mixtures of phases used for the calibration:

1. replicate analyses in the same laboratory should differ by no more than 1.1 percent (relative to the total clinker), and
2. each result should differ from the known value by no more than 1.8 percent (relative to the total clinker).

8. ACKNOWLEDGEMENTS

This report reflects the effort of those members of ASTM Task Group C01.23.01 who participated in the cooperative calibration. Work by CTL was supported by the Portland Cement Association under Project HA4003. We wish to acknowledge assistance by Fulvio Tang at the Construction Technologies Laboratory in preparing and analyzing the calibration phases and mixtures, and by John Mandel at NIST in the statistical analysis.

APPENDIX 1

Laboratories Participating in Cooperative Calibration

L.D. Adams
Southwestern Portland Cement
P.O. Box 937
Victorville, CA 92392

H. Chen
Canada Cement Lafarge Ltd. Research Center
6150 Royalmount
Montreal, Quebec, CANADA

J.T. Conway
Santee Cement Company
P.O. Box 698
Holly Hill, SC 29059

S. DeHayes/P. Hawkins
CalMat Co.
PO Box 947
Colton CA 92324

W. Gutteridge
British Cement Association
Wexham Springs
Slough, UK

H. Kanare/F. Tang
CTL, Inc.
5420 Old Orchard Road
Skokie, IL 60077

L. Keller
Camet Research Inc.
318 Twelfth St.
Santa Monica, CA 90402

G. McPherson
Halliburton Services
P.O. Box 1431
Duncan, OK 73536

B. Misteli
Holderbank
Technical Center
CH-5113 Holderbank, SWITZERLAND

APPENDIX 2

Summary of Results

2.1 Laboratory No. 1

2.1.1 Specified Method

Internal standard: TiO_2 , NIST SRM 674

Mixing method: Bleuler Mill, 1.7600 g mixture and 0.2400 g TiO_2

Instrument: computerized diffractometer

Peaks, (2θ) for Cu $K\alpha$:

orthorhombic C_3A : 21.0
 cubic C_3A : 21.8
 C_4AF : 44.2
 MgO: 42.9

Peak intensities: measured by computer

Results

(percent of mixture)
 Unknown 1 Unknown 2

cubic C_3A	21.1	62.4
	20.2	66.2
	21.4	64.1
orthorhombic C_3A	0.0	6.1
	0.0	0.5
	3.4	6.6
C_4AF	65.6	24.4
	62.1	24.8
	67.2	26.9
MgO	15.7	3.5
	16.1	3.5
	15.9	3.8

2.1.2 Additional Methods

Peak intensities measured manually

External standard (quartz, 36.5)

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C ₃ A	20.3	67.5
	20.5	67.6
orthorhombic C ₃ A	3.8	6.8
	2.6	6.9
C ₄ AF (24.3° peak)	65.3	21.5
	65.6	19.9
C ₄ AF (12.1° peak)	67.2	20.5
	66.2	20.6
MgO	15.3	3.9
	15.4	3.6

2.2 Laboratory No. 2

2.2.1 Specified Method

Internal standard: TiO_2 (rutile)

Mixing method: Spex Mixer Mill, 5 min

Instrument: computerized diffractometer

Peaks, (2θ) for Cu $K\alpha$:

orthorhombic C_3A : 20.56 - 21.33

cubic C_3A : 21.33 - 22.05

C_4AF : 23.60 - 24.89

MgO : 42.38 - 43.58

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	20.23	66.91
	21.15	63.60
	22.44	62.82
orthorhombic C_3A	-1.48	17.71
	2.61	14.72
	0.36	13.32
C_4AF	53.55	28.29
	59.13	28.69
	55.69	22.33
MgO	19.32	3.8
	20.61	3.46
	21.34	3.52

2.3 Laboratory No. 3

2.3.1 Specified Method

Internal standard: Si

Mixing method: ring-and-puck mill, 4.5000 g mixture, 0.5000 g Si, freon, 1 min

Instrument: computerized diffractometer (Rigaku)

Peaks, (2θ) for Cu K α :

orthorhombic C₃A: 48
cubic C₃A: 21.8
C₄AF: 12
MgO: 42.9

Peak intensities: measured by computer

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C ₃ A	21.	56.
	22.	71.
	31.	-5.
orthorhombic C ₃ A	30.	42.
	4.	4.
	12.	7.
C ₄ AF	57.	33.
	65.	22.
	52.	6.
MgO	28.	9.
	24.	9.
	30.	1.

Comments: noisy pattern with low peak/background ratio (for Unknown #2, the peak/background ratio for the C₄AF peak at 34° is 1.5; the ratio obtained by Laboratory 2 for the same peak is 63); no angle scale was provided, so peak positions and alignment cannot be assessed.

2.4 Laboratory No. 4

2.4.1 Specified Method

Internal standard: TiO_2 (rutile)

Instrument: computerized diffractometer (Siemens)

Peaks, (2θ) for Cu $K\alpha$:

all peaks for each phase in range 25° to 38°

Peak intensities: measured by computer

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	16.5	61.5
orthorhombic C_3A	8.5	13.0
C_4AF	54.0	22.5
MgO	21.5	4.0

2.5 Laboratory No. 5

2.5.1 Specified Method

Internal standard: Si, NIST SRM 640b

Mixing method: Bleuler Mill, 30 sec

Instrument: manual diffractometer (Philips)

Peaks, (2θ) for Cu $K\alpha$:

orthorhombic C_3A : 20.8

cubic C_3A : 21.6

C_4AF : 24.2

MgO: 42.8

Peak intensities: measured using planimeter

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	19.2	63.1
	20.0	62.3
	20.3	63.9
orthorhombic C_3A	10.4	10.7
	1.9	6.5
	0.0	8.4
C_4AF	55.5	26.2
	58.1	25.6
	56.6	26.4
MgO	19.4	4.4
	20.1	4.3
	18.8	4.3

2.6 Laboratory No. 6

2.6.1 Specified Method

Internal standard: Si (12 percent), NIST SRM 640b

Mixing method: Spex Mill, 1.0000 g mixture, 0.1200 g Si, and cyclohexane

Instrument: computerized diffractometer (Norelco)

Peaks, (2θ) for Cu $K\alpha$:

for each phase, all peaks within the region between 27° and 36° and the region between 39° and 49° .

Peak intensities: measured by computer using profile fitting algorithm (Savitzky and Golay)

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	18.	65.
	16.	56.
	18.	63.
orthorhombic C_3A	0.	11.
	0.	6.
	1.	5.
C_4AF	60.	21.
	49.	22.
	57.	25.
MgO	21.	3.
	18.	3.
	21.	5.

2.7 Laboratory No. 7

2.7.1 Specified Method

Internal standard: Si (12 percent)

Mixing method: Bleuler Mill, 1.0000 g mixture, 0.1200 g Si, and 5 ml 1,1,1-trichloroethane for 6 min

Instrument: computerized diffractometer (Philips APD 3600)

Peaks, (2θ) for Cu $K\alpha$:

orthorhombic C_3A : 21.0
cubic C_3A : 21.8
 C_4AF : 12.1
 C_4AF : 44.2
MgO: 42.9

Peak intensities: measured using profile fitting program QPROF

Results: normalized to 100 percent and averaged

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	19.	65.
orthorhombic C_3A	4.	6.
C_4AF	55.	25.
MgO	22.	4.

2.8 Laboratory No. 8

2.8.1 Specified Method

Internal standard: TiO_2 (12 percent), Rutile

Peaks, (2θ) for Cu $K\alpha$:

orthorhombic C_3A : 21.0
cubic C_3A : 22
 C_4AF : 24
 MgO : 43

Peak intensities: measured by computer

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	22.4	61.8
	20.8	66.2
	20.8	64.1
orthorhombic C_3A	-0.4	12.7
	0.9	10.9
	0.8	11.7
C_4AF	59.4	25.8
	54.1	27.5
	55.9	29.2
MgO	20.5	5.3
	18.9	5.0
	19.7	4.8

2.8.2 Additional Methods

External standard (CaF_2)

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	19.9	62.1
	18.2	61.0
	19.0	55.8
orthorhombic C_3A	1.1	4.2
	3.1	10.1
	2.4	12.7
C_4AF (12° peak)	55.0	22.6
	55.5	23.7
	55.8	21.8
MgO	19.4	4.5
	20.4	5.3
	17.9	4.4

2.9 Laboratory No. 9

2.9.1 Specified Method

Internal standard: Si (6 percent)

Instrument: Scintag, computerized diffractometer

Peaks, (2θ) for Cu $K\alpha$:

orthorhombic C_3A : 21.0
cubic C_3A : 21.8
 C_4AF : 24.3
MgO: 42.9

Peak intensities: measured by computer

Results

(percent of mixture)
Unknown 1 Unknown 2

cubic C_3A	25.0	87.2
	24.3	80.3
	21.8	74.9
orthorhombic C_3A	2.3	0.0
	0.0	0.0
	1.4	0.0
C_4AF	56.5	22.6
	53.4	31.6
	42.6	26.4
MgO	20.1	3.1
	24.9	3.9
	18.5	2.8

Appendix 3

Statistical Analysis

The statistical analysis was carried out according to ASTM E691. Of the nine participating laboratories, two were not included (Laboratory 4 and Laboratory 7) because they did not report replicate results.

The statistical analysis treated each phase as a separate material. This is legitimate even though the phases were determined using a single analysis, because each phase is estimated using a separate peak in the X-ray diffraction pattern.

Initial analysis (Tables 3-1 through 3-6) showed that h-values (Fig. 3-1) and k-values (Fig. 3-2) exceeded critical levels for several analyses by Laboratory 3. In addition, examination of the XRD patterns provided by this laboratory showed a considerably higher noise level and lower peak/background ratios compared to patterns of other participating laboratories. Therefore, it was decided that the results reported by Laboratory 3 were not representative of the consistency expected from this analysis, and the statistical analysis was repeated without Laboratory 3.

The analysis excluding Laboratory 3 (Tables 3-7 through 3-8) produced the following precision indices: 95 percent repeatability limit ($r = 2.8 \times s_r$) averaged 6.50 and ranged from 1.53 to 11.94; and 95 percent reproducibility limit ($R = 2.8 \times s_R$) averaged 10.53 and ranged from 2.23 to 22.19.

A graph of standard deviation levels versus average value (Fig. 3-3) indicates that standard deviation tended to increase slightly as the average value increased, but the correlation coefficients calculated using linear regression analysis (Table 3-9) were only 0.5 to 0.6. Therefore, it is tentatively concluded that the precision indices be calculated from the average value using the regression constants in Table 3-9.

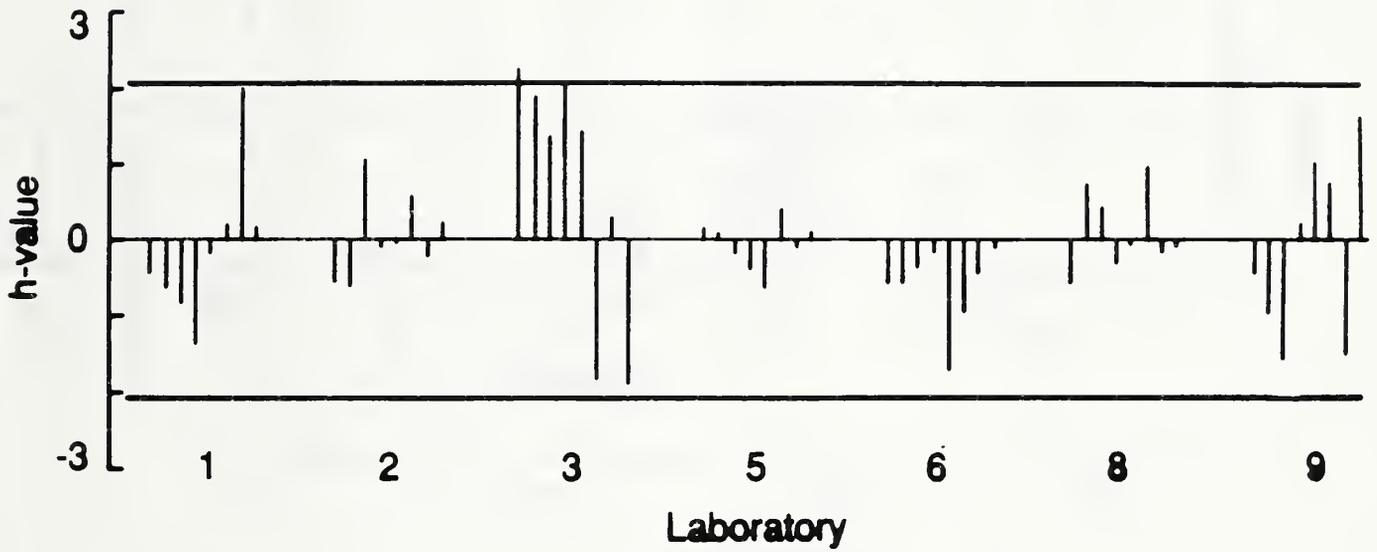


Figure 3-1. Level of h-value for each laboratory (critical values indicated by upper and lower horizontal lines).

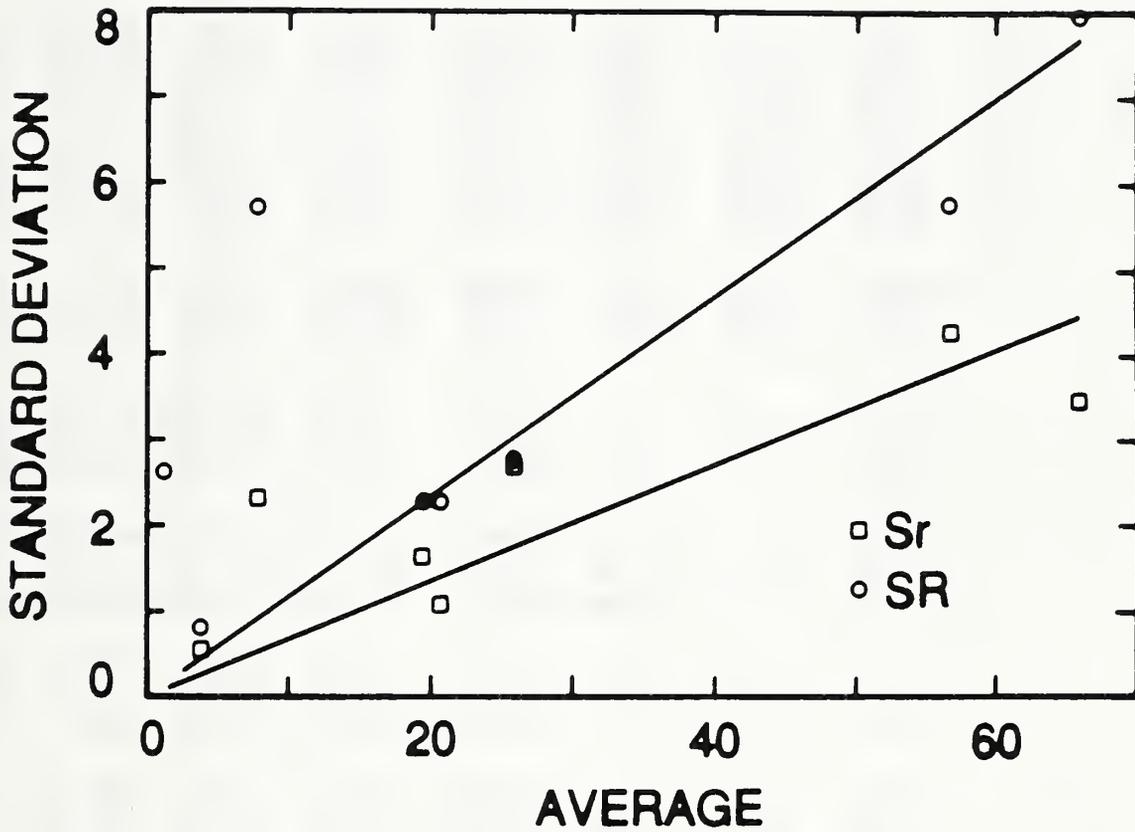


Figure 3-3. Standard deviation versus average value (relative to the mixture) for each phase in each unknown mixture, showing results of linear regression analysis (Table 3-9).

Table 3-1

QXRD Results for Statistical Analysis
(percent of mixture)

Unknown	or C ₃ A ^a 1	MgO 2	or C ₃ A 2	MgO 1	cu C ₃ A ^b 1	C ₄ AF 2	C ₄ AF 1	cu C ₃ A 2
Laboratory								
1	0.00	3.53	6.06	15.71	21.06	24.35	65.59	62.41
	0.00	3.53	0.53	16.12	20.24	24.76	62.12	66.24
	3.41	3.76	6.59	15.94	21.41	26.94	67.18	64.06
2	-1.48	3.80	17.71	19.32	20.23	28.29	53.55	66.91
	2.61	3.46	14.72	20.61	21.15	28.69	59.13	63.60
	0.36	3.52	13.32	21.34	22.44	22.33	55.69	62.82
3	30.00	9.00	42.00	28.00	21.00	33.00	57.00	56.00
	4.00	9.00	4.00	24.00	22.00	22.00	65.00	71.00
	12.00	1.00	7.00	30.00	31.00	6.00	52.00	-5.00
5	10.42	4.43	10.70	19.40	19.19	26.16	55.52	63.13
	1.86	4.29	6.48	20.13	20.04	25.62	58.10	62.28
	-0.04	4.34	8.39	18.83	20.26	26.38	56.59	63.87
6	0.00	3.00	11.00	21.00	18.00	21.00	60.00	65.00
	0.00	3.00	6.00	18.00	16.00	22.00	49.00	56.00
	1.00	5.00	5.00	21.00	18.00	25.00	57.00	63.00
8	-0.40	5.30	12.70	20.50	22.40	25.80	59.40	61.80
	0.90	5.00	10.90	18.90	20.80	27.50	54.10	63.00
	0.80	4.80	11.70	19.70	20.80	29.20	55.90	60.00
9	2.34	3.05	0.00	20.09	25.02	22.56	56.49	87.21
	0.00	3.87	0.00	24.87	24.29	31.62	53.38	80.31
	1.36	2.76	0.00	18.50	21.83	26.36	42.60	74.89

^aorthorhombic C₃A

^bcubic C₃A

Table 3-2

Cell Averages
(percent of mixture)

	or C ₃ A ^a 1	MgO 2	or C ₃ A 2	MgO 1	cu C ₃ A ^b 1	C ₄ AF 2	C ₄ AF 1	cu C ₃ A 2
Unknown								
Laboratory								
1	1.13	3.61	4.39	15.92	20.90	25.35	64.96	64.24
2	0.50	3.59	15.25	20.42	21.27	26.44	56.12	64.44
3	15.33	6.33	17.67	27.33	24.67	20.33	58.00	40.67
5	4.08	4.35	8.53	19.45	19.83	26.05	56.73	63.09
6	0.33	3.67	7.33	20.00	17.33	22.67	55.33	61.33
8	0.43	5.03	11.77	19.70	21.33	27.50	56.47	61.60
9	1.23	3.23	0.00	21.15	23.71	26.85	50.82	80.80
\bar{x}^c	3.29	4.26	9.28	20.57	21.29	25.03	56.92	62.31
$s_{\bar{x}}^d$	5.47	1.10	6.14	3.42	2.42	2.59	4.21	11.70

^aorthorhombic C₃A

^bcubic C₃A

^coverall average of cell averages

^dstandard deviation of cell averages

Table 3-3

Cell Standard Deviations
(percent of mixture)

	Unknown	or C ₃ A ^a 1	MgO 2	or C ₃ A 2	MgO 1	cu C ₃ A ^b 1	C ₄ AF 2	C ₄ AF 1	cu C ₃ A 2
Laboratory									
1		1.97	0.14	3.36	0.21	0.60	1.39	2.59	1.92
2		2.05	0.18	2.24	1.02	1.11	3.56	2.82	2.17
3		13.32	4.62	21.13	3.06	5.51	13.58	6.56	40.25
5		5.57	0.07	2.11	0.65	0.56	0.39	1.30	0.80
6		0.58	1.15	3.21	1.73	1.15	2.08	5.69	4.73
8		0.72	0.25	0.90	0.80	0.92	1.70	2.70	1.51
9		1.18	0.58	0.00	3.32	1.67	4.55	7.28	6.17
s _r ^c		5.59	1.83	8.27	1.91	2.31	5.69	4.66	15.55

^aorthorhombic C₃A

^bcubic C₃A

^crepeatability standard deviation

Table 3-4

Between-Laboratory Consistency Statistic Values
(h-statistic)
(percent of mixture)

Unknown	or C ₃ A ^a 1	MgO 2	or C ₃ A 2	MgO 1	cu C ₃ A ^b 1	C ₄ AF 2	C ₄ AF 1	cu C ₃ A 2
Laboratory								
1	-0.39	-0.59	-0.79	-1.36	-0.16	0.13	1.91	0.16
2	-0.51	-0.61	0.97	-0.04	-0.01	0.54	-0.19	0.18
3	2.20	1.89	1.37	1.98	1.39	-1.81	0.26	-1.85
5	0.14	0.09	-0.12	-0.33	-0.60	0.40	-0.04	0.07
6	-0.54	-0.54	-0.32	-0.17	-1.63	-0.91	-0.38	-0.08
8	-0.52	0.71	0.41	-0.25	0.02	0.96	-0.11	-0.06
9	-0.38	-0.94	-1.51	0.17	1.00	0.70	-1.45	1.58
Critical	2.05							

^aorthorhombic C₃A

^bcubic C₃A

Table 3-5

Within-Laboratory Consistency Statistic Values
(k-statistic)
(percent of mixture)

	or C ₃ A ^a	MgO	or C ₃ A	MgO	cu C ₃ A ^b	C ₄ AF	C ₄ AF	cu C ₃ A
Unknown	1	2	2	1	1	2	1	2
Laboratory								
1	0.35	0.07	0.41	0.11	0.26	0.24	0.56	0.12
2	0.37	0.10	0.27	0.54	0.48	0.63	0.60	0.14
3	2.38	2.54	2.56	1.60	2.39	2.38	1.41	2.59
5	1.00	0.04	0.26	0.34	0.24	0.07	0.28	0.05
6	0.10	0.64	0.39	0.91	0.50	0.37	1.22	0.30
8	0.13	0.14	0.11	0.42	0.40	0.30	0.58	0.10
9	0.21	0.32	0.00	1.74	0.72	0.80	1.56	0.40
Critical	2.02							

^aorthorhombic C₃A

^bcubic C₃A

Table 3-6

Summary of Precision Parameters
(percent of mixture)

Phase	Unknown	s_r^a	s_R^b
orthorhombic C ₃ A	1	5.59	7.12
MgO	2	1.82	1.84
orthorhombic C ₃ A	2	8.27	9.13
MgO	1	1.91	3.76
cubic C ₃ A	1	2.31	3.07
C ₄ AF	2	5.69	5.69
C ₄ AF	1	4.66	5.68
cubic C ₃ A	2	15.55	17.26

^arepeatability standard deviation

^breproducibility standard deviation

Table 3-7

Cell Averages Excluding Laboratory 3
(percent of mixture)

	Unknown	or C ₃ A ^a 1	MgO 2	or C ₃ A 2	MgO 1	cu C ₃ A ^b 1	C ₄ AF 2	C ₄ AF 1	cu C ₃ A 2
\bar{x}^c		1.29	3.92	7.88	19.44	20.73	25.81	56.74	65.92
$s_{\bar{x}}^d$		1.42	0.66	5.37	1.83	2.10	1.70	4.58	7.41

^aorthorhombic C₃A

^bcubic C₃A

^coverall average of cell averages

^dstandard deviation of cell averages

Table 3-8

Summary of Precision Parameters Excluding Laboratory 3
(percent of mixture)

Phase	Unknown	s_r^a	s_R^b
orthorhombic C ₃ A	1	2.63	2.63
MgO	2	0.55	0.80
orthorhombic C ₃ A	2	2.31	5.69
MgO	1	1.64	2.26
cubic C ₃ A	1	1.07	2.27
C ₄ AF	2	2.67	2.76
C ₄ AF	1	4.26	5.75
cubic C ₃ A	2	3.46	7.93

^arepeatability standard deviation

^breproducibility standard deviation

Table 3-9

Linear Regression, Standard Deviation Versus Average

	intercept (percent of mixture)	slope	Correlation (R^2)
S_I	1.40	0.037	0.52
S_R	1.86	0.075	0.56

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET <i>(See instructions)</i>	1. PUBLICATION OR REPORT NO. NISTIR 89-4164	2. Performing Organ. Report No.	3. Publication Date SEPTEMBER 1989
4. TITLE AND SUBTITLE Cooperative Calibration and Analysis of Cement Clinker Phases			
5. AUTHOR(S) Leslie Struble; H. Kanare			
6. PERFORMING ORGANIZATION <i>(If joint or other than NBS, see instructions)</i> NATIONAL BUREAU OF STANDARDS U.S. DEPARTMENT OF COMMERCE GAITHERSBURG, MD 20899		7. Contract/Grant No.	8. Type of Report & Period Covered
9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS <i>(Street, City, State, ZIP)</i>			
10. SUPPLEMENTARY NOTES <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
11. ABSTRACT <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> <p>An interlaboratory calibration and analysis has been carried out by ASTM Task Group C01.23.01 to assess the use of quantitative X-ray diffraction analysis to determine the proportion of phases in portland cement clinker. This interlaboratory test provides an estimate of precision and bias in the quantitative phase analysis of some clinker phases in mixtures prepared using calibrating phases. These estimates of precision and bias will be incorporated in a proposed standard test method on quantitative phase analysis of cement and clinker currently being developed by the task group.</p>			
12. KEY WORDS <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> cement; clinker; interlaboratory calibration; phase analysis; X-ray diffraction			
13. AVAILABILITY <input type="checkbox"/> Unlimited <input checked="" type="checkbox"/> For Official Distribution. Do Not Release to NTIS <input type="checkbox"/> Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. <input type="checkbox"/> Order From National Technical Information Service (NTIS), Springfield, VA. 22161		14. NO. OF PRINTED PAGES 51	15. Price

3. 1990.